Clean and highly ordered graphene synthesized in the gas phase

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We report that the substrate-free gas-phase graphene synthesis method produces clean and highly ordered graphene sheets that are similar in quality to the graphene obtained through the mechanical exfoliation of highly oriented pyrolytic graphite.

The presence of lattice imperfections and oxygen functionalities on a graphene sheet define its quality. Clean and highly ordered graphene exhibits extremely high room-temperature carrier mobility[1,2] and thermal conductivity,[3] and these remarkable properties are very sensitive to defects and disorder.[4] Recent experiments have demonstrated that the formation of defects on pristine sheets results in electrically and thermally insulating behavior.[5] Furthermore, the bonding of oxygen to graphene in the form of functional groups, such as carboxyl and hydroxyl, has a detrimental effect on its electronic structure.[6–8] For example, graphene is a nearly metallic material, while graphene oxide is an insulator.[6] Graphene of the highest quality can be obtained by mechanically exfoliating highly oriented pyrolytic graphite (HOPG), but the fact that the approach is not scalable for commercial applications has driven the search for an alternative technique that is capable of obtaining high yields of clean and highly ordered graphene.

Although numerous graphene synthesis methods have been developed in recent years, current approaches produce sheets that are much lower in quality than mechanically exfoliated graphene.[7–16] The chemical reduction of graphene oxide can be scaled up for mass production, but the resulting sheets exhibit defects, disorder, and adsorbed functional groups.[9] The exfoliation–reintercalation–expansion of graphite has yielded graphene that is less disordered than what is obtained through chemical reduction, but C–O, C–H, and O–H bonds are present on the sheets.[7] The dispersion of graphene oxide paper in pure hydrazine can create micron-sized graphene flakes, but the samples obtained were disordered and elemental analysis revealed that the sheets contained 9% O by mass.[8] The low-temperature flash pyrolysis of a solvothermal product of sodium and ethanol can produce gram-scale quantities of graphene,[10] but the sheets are highly defective and contain even larger quantities of oxygen (18% O by mass). Large-area graphene has been created by chemical vapor deposition (CVD), but this method is dependent on the quality of an underlying polycrystalline metallic film, and thus the resulting sheets are relatively disordered and consist of regions of varying numbers of graphene layers.[11,12] Few-layer, rotationally disordered sheets obtained through the vacuum graphitization of SiC exhibit the electronic properties of graphene,[13] but the approach yields graphene layers with small domains,[14] and the high temperatures and ultrahigh vacuum conditions necessary for growth limit the use of this technique in large-scale applications.[11] Furthermore, graphene synthesized on substrates by epitaxy[15] and CVD[11,12] requires multiple processing steps, such as wet-etching and micro-fabrication, to obtain transferable sheets.

Recently, the substrate-free gas-phase synthesis of free-standing graphene sheets was achieved.[17] This single-step method is capable of continuous graphene production at ambient conditions. The technique involves sending an aerosol consisting of liquid ethanol droplets and argon gas directly into an atmospheric-pressure microwave-generated argon plasma. Over a time scale on the order of 10^{-1} s, ethanol droplets evaporated and dissociated in the plasma, forming solid matter (Fig. 1a). Previously, characterization by transmission electron microscopy (TEM) and Raman spectroscopy proved that this approach forms graphene.[17] In this study, the quality of the synthesized graphene sheets was determined using Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), elemental analysis by combustion, and an aberration-corrected transmission electron microscope (TEAM 0.5), which is capable of clearly resolving individual carbon atoms, defects, and adsorbates on graphene at an accelerating voltage of 80 kV.[4]

No post-synthesis treatments, such as chemical reduction, dispersion in liquids, or thermal annealing, were carried out after samples were obtained. TEM specimens were prepared by depositing the as-synthesized graphene directly onto commercially available TEM grids (Ted Pella, lacey carbon 300 mesh Cu grids). Following a similar preparation procedure used in FT-IR studies of graphite oxide[18] and graphene,[7] synthesized sheets were mixed with KBr powder and compressed into a transparent tablet for measurements. The FT-IR spectrum (400–4000 cm^{-1}) of the synthesized graphene was measured using a Nicolet 6700 spectrometer with pure KBr as the background. As-synthesized graphene sheets were deposited onto a Si substrate for XPS analysis, which was conducted using a PHI 5400 ESCA/XPS using an Al Kα radiation source. The spot size used was 1.1 mm in diameter.

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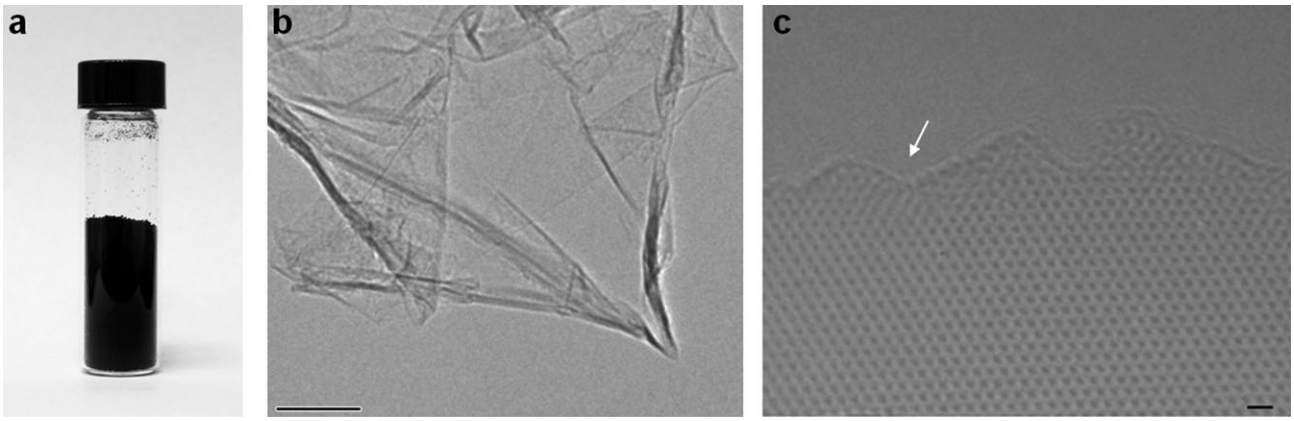

Fig. 1 (a) A 6 cm tall vial containing a 100 mg sample. In our current experimental setup, samples were obtained at a rate of 2 mg min^{-1}. (b) A typical low-magnification TEM image of synthesized graphene sheets. Scale bar is 100 nm. (c) A high-resolution image directly taken at 80 kV in the TEAM 0.5. The white arrow indicates the edge of the sheet. Scale bar is 4 Å.

A Zeiss Libra 200/FEG TEM was used to obtain a low-magnification image of synthesized graphene at 200 kV. Individual sheets typically appear folded and overlapping in low-magnification images, and are as large as several hundred nm (Fig. 1b). A high-resolution direct image of a synthesized sheet, taken using the TEAM 0.5 (Fig. 1c), shows the hexagonal arrangement of carbon atoms that is characteristic of graphene.[4] The sheet is highly ordered and free of adsorbates, even in the region near the edge.

An atomic-resolution TEAM 0.5 image reveals a highly ordered synthesized single-layer graphene sheet (Fig. 2). Individual carbon atoms appear white in the image, and are arranged in a hexagonal pattern with a 0.14 nm bond length. Prior to this study, such a clean and structurally perfect single-layer sheet had only been observed from graphene obtained from graphite.[4]

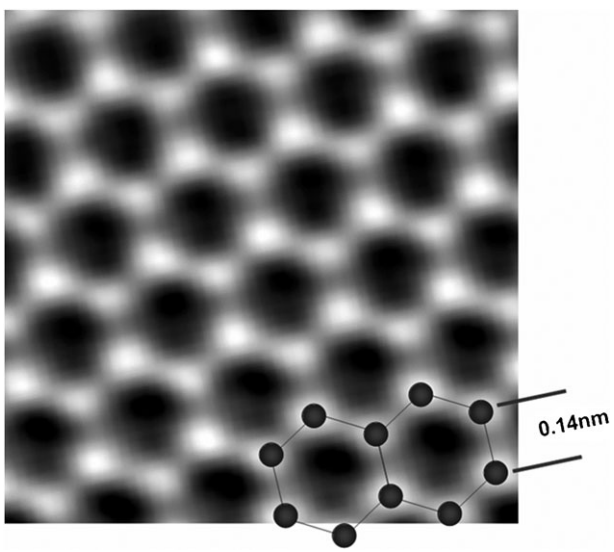

Fig. 2 An atomic-resolution image of a clean and structurally perfect synthesized graphene sheet. Individual carbon atoms appear white in the image. The image was obtained through the reconstruction of the electron exit wave function from 15 lattice images using MacTempas software.

FT-IR has been used to detect the presence of functional groups on graphene oxide and chemically exfoliated graphene.[7,9,18] Prominent features in the FT-IR spectrum of electrically insulating graphene oxide[9] include absorption bands corresponding to C–O stretching at 1053 cm^{-1}, C–OH stretching at 1226 cm^{-1}, phenolic O–H deformation vibration at 1412 cm^{-1}, C=C ring stretching at 1621 cm^{-1}, C=O carbonyl stretching at 1733 cm^{-1}, and O–H stretching vibrations at 3428 cm^{-1}. Additionally, one CH_3– and two CH_2– peaks occur at 2960, 2922, and 2860 cm^{-1}, respectively.[18] These features are either absent or minimal in the FT-IR spectrum of the synthesized graphene (Fig. 3a). To verify these findings, an FT-IR spectrum of ball-milled HOPG was obtained for comparison. The HOPG powder exhibited weak absorption bands at 1200 and 1580 cm^{-1}, in agreement with published transmission spectra of graphite that had been extensively milled.[19] The strong similarity between the FT-IR spectra of the synthesized graphene and HOPG (Fig. 3a, inset) and the absence of other features showed that the sheets were free of functional groups.

Additional elemental characterization studies confirmed the FT-IR results. An XPS spectrum obtained from the synthesized sheets (Fig. 3b) also resembles spectra obtained from HOPG.[7] Elemental analysis by combustion,[20] which measured C, H, and N, revealed that the mass composition of the as-synthesized graphene was 98.9% C, 1.0% H, and 0.0% N (0.1% O by difference). A direct measurement of oxygen also showed that the sheets had a mass composition of 0.1% O. These results show that oxygen from the ethanol does not bond to the graphene during the synthesis process.

The substrate-free gas-phase method can continuously produce clean and highly ordered free-standing graphene sheets. Milligram amounts of graphene can be collected in minutes with the current experimental setup,[17] and it is possible to scale up the process to obtain industrial quantities. We suggest that the graphene synthesized by this method can substantially enable graphene research and applications.

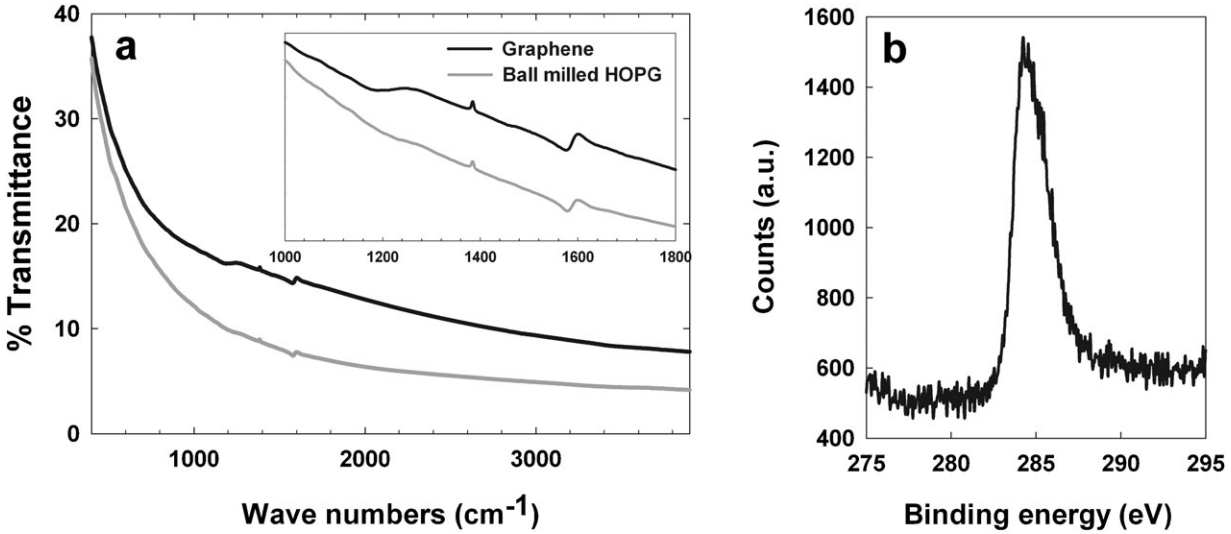

Fig. 3 (a) An FT-IR spectrum of the synthesized graphene. Peaks corresponding to detrimental functional groups are either absent or not prominent in the spectrum. Also shown is the FT-IR spectrum obtained from ball-milled HOPG. The similar features of the HOPG powder and synthesized graphene are shown in the inset. (b) An XPS spectrum of the synthesized graphene.

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